

- Project Background
- Acceleration
- Emissions
- Braking
- Fuel Economy
- Cold Start
- Driveability and Handling



Chassis Dynamometer Emissions Testing

The emissions test procedure was performed twice for each test vehicle on each appropriate test fuel. The order of testing the fuels in a flexible- or bi-fuel test vehicle was randomly selected. The overall test sequence consisted of a fuel change procedure and the exhaust emissions portion of the Federal Test Procedure (FTP). The exhaust emissions FTP was performed following EPA certification procedures and tolerances.

After mileage accumulation but prior to testing, the vehicles were equipped to drain the on-board fuel through the fuel rail drain by actuating the electric fuel pump. Liquid fuel tank thermocouples were installed in each vehicle in a manner that did not leave wires or fittings exposed.

Fuel Change Procedure for Emissions Tests

The Auto/Oil Air Quality Improvement Research Program (AQIRP) fuel change procedure was used prior to each emissions test. The procedure is designed to minimize fuel carryover effects by thoroughly flushing the fuel delivery system and also to precondition the canister to the new fuel. The AQIRP preconditioning sequence consists of a 60-min, 40 cubic feet per hour canister purge, a drain and 3-gal fill with room temperature test fuel, a 1-min idle, a drain and 40% tank volume fill with cold fuel, and an unsampled diurnal heat build (to load the canister with test fuel vapor). These steps are followed by an Urban Dynamometer Driving Sequence (UDDS) preconditioning drive (to allow the vehicle's computer to "learn" the new fuel) and key off/idle sequence prior to re-entry into the standard FTP preconditioning. For a more detailed illustration of this procedure, [a fuel change procedure flow chart](#) is available.

Emissions Test Procedure

Following preconditioning, vehicles entered a 12- to 36-h key-off, temperature-controlled soak at 75 degrees F. At the end of the soak period, the vehicles were placed on a dynamometer for the beginning cold-start (Bag 1) portion of the FTP exhaust emissions test. For alcohol-fueled test vehicles, the tail-pipe connector, all sample lines, and the dilution air were heated to prevent condensation losses. A dilute sample was drawn through impingers for determination of alcohols and/or carbonyls when appropriate. Speciation bags were analyzed within 4 h to maintain sample integrity.



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The first phase of the exhaust test was followed immediately by the cold stabilized portion (Bag 2) and, after a 10-min engine shutdown, the hot-start test (Bag 3). Alcohol-carbonyl sampling of dilute exhaust occurred during each of the three FTP test phases. A single background sample was taken during the FTP test. Parallel dilute exhaust and background sample bags were also drawn for each test phase. These bags were analyzed immediately for hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO₂), oxides of nitrogen, (NO_x), and methane (CH₄).

Re-Test Criteria for Emissions Tests

To ensure accurate emissions results, a re-test criterion was used for each pair of emissions tests. This criterion was used to determine if a third emissions test was necessary, and was based on a similar criterion developed during the AQIRP.

The re-test ratios used for FTP composite emissions results were:

- HC greater than 1.175
- CO greater than 1.336
- NO_x greater than 1.40
- mpg greater than 1.045

The ratio is defined as the larger test value divided by the smaller test value. Technicians performed a third test if any of the above tail-pipe mass emission conditions were found.

Chemical Speciation

The emissions test lab's hydrocarbon method used Varian™ 3600 gas chromatographs (GCs) with dual injectors, columns, and flame ionization detectors, allowing two similar analyses to be run simultaneously. A comparison of the total hydrocarbon determined using the GC versus the constant volume sampler (CVS) "speciation recovery" was used as a quality control measure. A 23 hydrocarbon standard mixture "CRC-4" (Coordinating

Research Council #4 gas calibration mixture from Scott Specialty Gases, Troy, Mich.) was analyzed at the start of each day on each GC to provide quantifying coefficients and a quality control check on daily reproducibility of instrument performance.

In the single-GC method, all components were separated using one column type and temperature program. Analysis time for a cycle was 65 min. Each exhaust or evaporative gas sample was simultaneously injected (using a single sampling from the bag) into identical columns residing in the dual column GC. Column A contains a 85-mL sample loop (splitless injection) that provides an injection volume small enough to allow resolution of the C1 through C4 hydrocarbons, but large enough to retain the highest sensitivity possible. Column B receives a 1000-mL splitless injection, providing higher sensitivity for components eluting after isobutane. Quantitative comparison of three overlap components (butane, isopentane, and pentane) provides a quality control measure. Data from column A are used to detect and quantitate the 12 earliest eluting hydrocarbons with detection limits of 15-25 ppbVC, corresponding to 0.2-0.3 mg/mi hydrocarbon for FTP stages 1 and 3, and 0.3-0.5 mg/mi for FTP stage 2. Data from column B give detection limits 0.017-0.04 mg/mi HC for components eluting after isopentane (18th in elution order). The components eluting between the 9th and 18th in elution order have detection limits ranging between the levels listed above for each column. Typical detection limits were determined to be between 0.02 and 0.06 mg/mi for the toxics 1,3-butadiene and benzene.

Aldehyde and alcohol sampling for tests with alcohol containing fuels is made difficult by the large amount of water in the exhaust gases. Prevention of condensation in the CVS and all other associated equipment that contacts the exhaust gas (both before and after dilution), is absolutely critical to achieving acceptable aldehyde recoveries. The emissions test lab has installed special equipment for the complete elimination of condensation with alcohol fuels. This includes heating provisions for the CVS, dilution air, exhaust pipe connectors, CVS sample bags, impinger apparatus plumbing, and all the lines that convey CVS diluted gases to sampling or analysis points. Spiking recovery experiments are periodically performed whenever alcohol fuel testing is conducted to validate alcohol and aldehyde sampling performance.

Aldehydes and ketones in exhaust emissions were sampled using tandem liquid impingers, which trap them as 2,4-dinitrophenylhydrazones (DNPH) derivatives. These derivatives were analyzed by high-performance liquid chromatography (HPLC) with ultra-violet absorbance detection. The method used was essentially identical to the current state-of-the-art as reflected by the methods currently in use by the EPA, the AQIRP, and the California Air Resources Board (CARB Method 1004). Calibration standards were analyzed before and after each test series. This system provides detection limits of 0.10 mg/mi for formaldehyde and 0.16 mg/mi for acetaldehyde for FTP phase 1 samples.

Alcohols in exhaust and evaporative emissions were collected in tandem reagent water impingers held at ice temperature. After sampling, the impinger fluid was spiked with an internal standard (n-propanol) for quantitation. These samples were then analyzed using a Varian 3600 GC equipped with an autosampler, a 30-m, 0.53-mm ID fused silica column

with a 5.0-mm polydimethylsiloxane film, and a flame ionization detector. All aspects of the sample collection and analysis are functionally equivalent to the methods currently in use by the EPA, the Auto Oil AQIRP, and the CARB (Method 1001). The only differences are in the use of a chromatographic retention gap, choice of the internal standard, and the carrier gas flow rate and oven temperature program. All these have been optimized for better performance than the referenced methods. The separation of methanol and ethanol was accomplished using a single column, exhibiting detection limits of 2.5 mg/mi for methanol and 1.3 mg/mile for ethanol for an FTP phase 1 cycle.

Speciation tests performed included alcohol (alcohol fuel tests only), aldehyde/ketone, and hydrocarbon speciation. The chemical species included in the speciation analyses were benzene, 1,3-butadiene, formaldehyde, and acetaldehyde. Alcohol was quantified for the tests on alcohol fuel vehicles only.

Potency Weighted Toxic Emissions

Air toxics are pollutants that have been classified by EPA as known or probable human carcinogens (in other words, components considered to have adverse affects on human health). The air toxics included in the study are benzene (C₆H₆, a known carcinogen), as well as formaldehyde (HCHO), acetaldehyde (CH₃CHO), and 1,3-butadiene (C₄H₆), all probable carcinogens. These compounds are reported as potency weighted toxics (Pwt). The EPA has calculated an inhalation unit risk factor for each hazardous compound. The four compounds listed here are given a weighing factor by comparing each compound's unit risk factor to the unit risk factor that was the highest of the four (1,3-butadiene). This factor is multiplied by the mass emissions for that compound, which gives the potency weighted toxic value. The total Pwt is the sum of the four toxics.

Unit Risk and Weighted Factors

Compound	EPA Risk (μg/m ³)- ¹	EPA weighted factor
1,3-butadiene	2.8E-4	1.0
benzene	8.3E-6	0.030
formaldehyde	1.3E-5	0.046
acetaldehyde	2.2E-6	0.008

[\[HOME\]](#) [\[TOP OF PAGE\]](#)